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**NASA CONTRACTOR  
REPORT**



**NASA CR-54**

**NASA CR-54**

269

N64-24826

Vol 1

Lot 29

# **STUDY IN COMETARY ASTROPHYSICS**

*by Vincent J. DeCarlo*

Prepared under Contract No. NASw-589 by

MELPAR, INC.

Falls Church, Virginia

for

**NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • JULY 1964**

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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## I. INTRODUCTION

An experimental program has been initiated to develop some understanding of the chemical and physical processes that can occur in comets and which account for their activity. The mechanisms of the processes occurring in cometary materials may also aid in explaining the formation and evolution of the solar system, as well as the behavior of other materials placed in space for various experimental missions.

Comets are composed of three parts: (1) coma, (2) tail, and (3) nucleus. The coma has been studied by recording the emissions from the atoms and radicals (Na, O, CN, CH, OH, NH, C<sub>2</sub>, C<sub>3</sub>, NH<sub>2</sub>) that fluoresce as they absorb electromagnetic radiation from the sun. Emissions from the tail show only the presence of the ionized molecules CO<sup>+</sup>, N<sub>2</sub><sup>+</sup> and CO<sub>2</sub><sup>+</sup>. The nucleus is the source of all molecular species found in the coma and tail of the comet. Information concerning the nucleus is very limited, and models have been proposed by Whipple<sup>1</sup> and by Donn and Urey.<sup>2</sup>

The Whipple model is an icy-conglomerate of a loosely-bound solid at low temperature. The solid for the major portion is composed of H<sub>2</sub>O, CH<sub>4</sub> and NH<sub>3</sub>. Donn and Urey enlarged this model by including the reactive molecules of H<sub>2</sub>O<sub>2</sub>, C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> and the free radicals of NH, CH, OH, etc. to account for the high activity of comets. These two models have given the necessary direction to the current laboratory research program.

- 
1. Whipple, F. L., *Astrophys. J.* 111, 375 (1950).
  2. Donn, B. and Urey, H. C., *Mem. Soc. roy. Sci. Liege*, Collection in 4° 18, 124 (1957).

## II. EXPERIMENTAL STUDY

The experimental program has been directed toward the production of the spectra observed in the comet head. The present investigations were divided into two areas, (1) the vacuum ultraviolet photolysis of gases at low pressure and, (2) the ultraviolet photolysis of low temperature solids.

### A. Vacuum Ultraviolet Photolysis

#### 1. Apparatus and Equipment

Vacuum System: The vacuum apparatus used for these experiments was of conventional design with suitable pumps, gauges, liquid nitrogen traps, and gas storage bulbs.

Photolysis Cell: The cell was constructed with an entrance window (LiF) at right angles to an exit quartz window. Opposite each window was a horn-shaped tube for trapping scattered light. The cell was painted with several coats of flat, black paint. The LiF windows became coated very rapidly in the acetylene experiments and for ease of replacement, were mounted on shortened 24/40 ground joints.

Light Source: The lamps were constructed of 12 mm OD quartz with 25 mm flared front. The LiF was cemented to the quartz with either (1) Apiezon W-100 medium hard wax, (2) Ag-AgCl seal or, (3) epoxy cement. The cleaved plates were 2 mm thick, 25 mm in diameter, and obtained from Harshaw Chemical Co. The lamps contained 1 mm of krypton; during excitation the end of the lamp was immersed in liquid nitrogen to remove impurities that could be produced from the walls during discharge. Lamps with barium getters were also constructed and used. Electrodeless excitation of the lamp was produced by a Raytheon 2450 mc microwave generator.

Monochromator and Spectrographs: A Bausch and Lomb monochromator, with either a 1P21 or 1P28 photomultiplier tube, was used to monitor emissions. The spectrographs used were either (1) Hilger and Watts Raman, (2) Bass-Kessler,<sup>3</sup> or (3) Jarrel-Ash automatic recording monochromator.

Chemicals: Phillips research grade methane, ethane, and ethylene were used without further purification. Acetylene was obtained from Matheson and purified by trap-to-trap distillation in vacuo. Mass spectrometric analysis of both gases showed them to be at least 99.5 percent pure with no detectable aromatic impurities. Carbon suboxide was prepared by the dehydration of malonic acid with phosphorus pentoxide at 140°C<sup>4</sup>. Mass spectrometric analysis verified the product purity to be better than 99 percent. Research grade oxygen, nitrogen, krypton, and xenon were obtained from Air Reduction, Inc., and used without purification.

## 2. Experimental Procedure

All experiments were started when the system was evacuated to better than  $2 \times 10^{-5}$  mm Hg. The gas to be studied was measured in the photolysis cell with a CVC Autovac Gauge.

The emission was recorded on an Aminco microphotometer as percent transmission. The readings were taken at various pressure and wavelength settings in a random order, eliminating any possible effect due to the length of time the sample was subjected to photolysis. The empty cell was

3. Bass, A. M. and Kessler, K. G., J. Opt. Soc. Am. 49, 1223-5 (1959).

4. Long, D. A., Murfin, F. S. and Williams, R. L., Proc. Roy. Soc. A. 223, 242 (1954).

checked before each experiment for lamp scattering. The scatter accounted for only a few percent of the emission level observed from acetylene and this was subtracted from the measurements.

There were a number of long experiments with the spectrographs that required constant changing of the LiF window in the cell and lamps. The cell windows required changing at the end of one hour and the lamp windows required changing at the end of three hours of photolysis. Before the cell was placed in position with the spectrograph the total level of emission from the cell was measured by photoelectric detection.

### 3. Results

Emission has been observed for methane and acetylene but not for ethane, ethylene, carbon suboxide, nitrogen or oxygen.

The emission from methane was at a very low light level and in these experiments the intensity of scatter was comparable in size to the emission. Thus, large exit and entrance slits of the monochromator were required to detect the emission, and this made it difficult to develop very much detail in the observed emission. However, the emission occurred in the region  $5300\text{\AA}$  to  $6000\text{\AA}$  and at pressures between 0.01 mm and 1 mm Hg. Maximum intensity of the emission occurred at about 0.1 mm pressure, with gradual decrease in intensity at both lower and higher pressures of methane. Addition of 2 mm of nitrogen to 0.1 mm  $\text{CH}_4$  completely eliminated the emission. This indicates that the decrease in the intensity of the emission at higher pressures of pure methane was probably a physical quenching effect. The decrease in the intensity of the emission at pressures lower than 0.1 mm was most probably due to the decreased absorption of the vacuum ultraviolet radiation by the methane.



A series of experiments were performed to establish that the increased light emitted upon the introduction of methane was due to emission from the methane following absorption of the vacuum ultraviolet light and not due to scattered light from the lamp. These experiments showed that it was impossible to distinguish, at any wavelength, between the intensity of visible scatter observed from the lamp with an evacuated cell and that observed with (1) the unfiltered light and cell containing 2 mm of nitrogen, (2) the vacuum ultraviolet filtered out by quartz and the cell containing 0.1 mm  $\text{CH}_4$ , and (3) the unfiltered light and cell containing 0.1 mm  $\text{CH}_4$  and 2 mm of nitrogen. This clearly demonstrates the necessity for the presence of methane at relatively low pressure and the presence of vacuum ultraviolet radiation in order for the emission to be observed. The intensity level for this emission was about 4 percent of the acetylene emission and about 1 percent of OH emission from water under identical conditions.

The emission from acetylene was about 25 times the methane level and about 20 percent of the OH emission from water. The emission occurred in the region  $4500\text{\AA}$  to  $6000\text{\AA}$  and has been observed from  $10^{-3}$  to 4 mm Hg with the maximum occurring at 0.1 mm and  $4950\text{\AA}$ . The emission was lost by insertion of quartz for the LiF window or by using a xenon resonance lamp instead of the krypton lamp. Both 1P21 and 1P28 phototubes indicated that the maximum occurred at  $4950\text{\AA}$ . Photometric tracing of the emission is shown in figure 1 using the Bausch and Lomb monochromator.

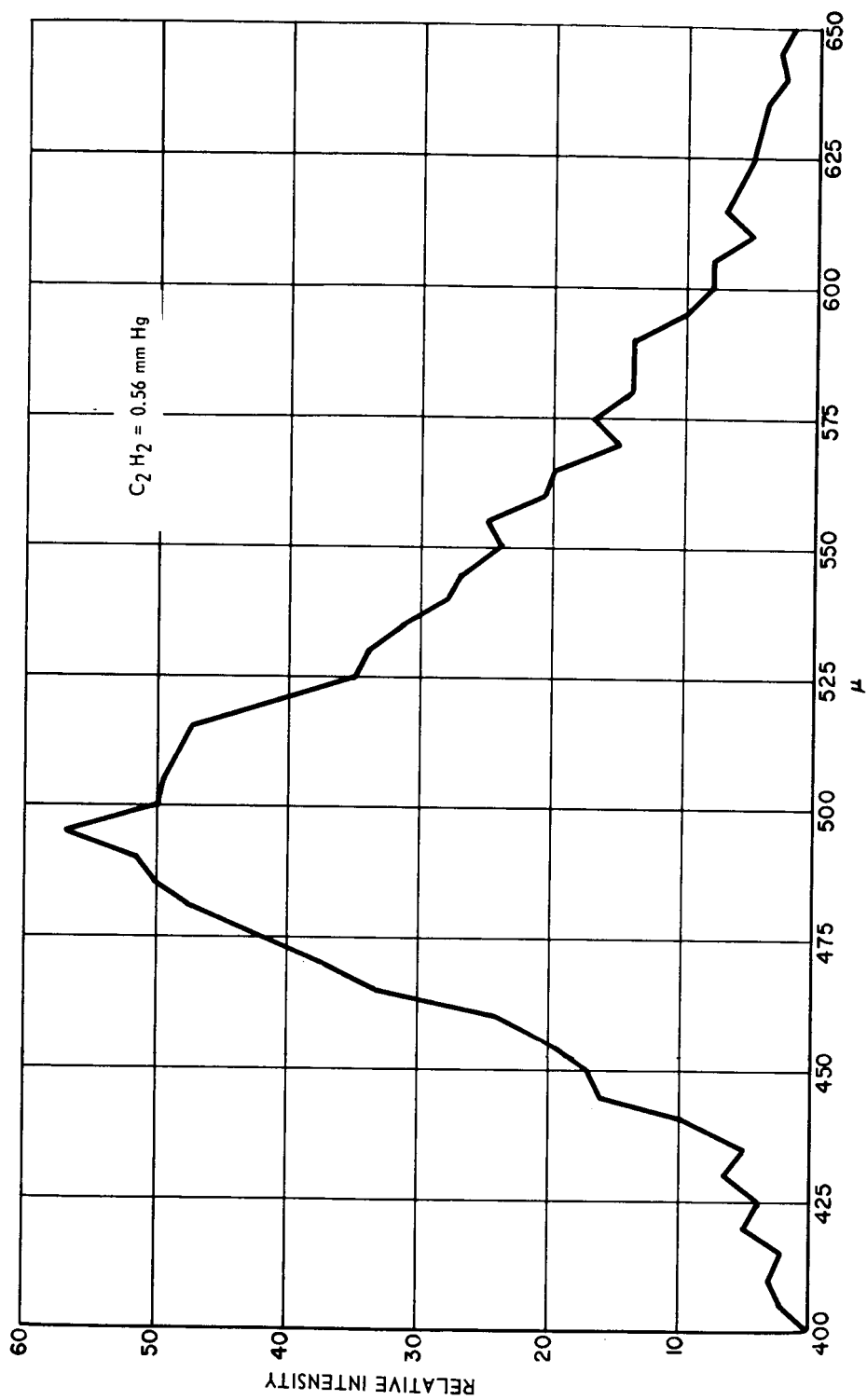


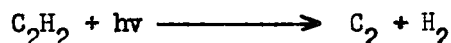
Figure 1. Acetylene Emission

Because the acetylene emission was higher than the methane emission, experiments were undertaken to photograph the emission from acetylene. The longest experiment attempted had twenty hours exposure on a Kodak 103a 0 plate, using the Raman spectrograph. No conclusive structure was obtained. The Bass-Kessler spectrograph is faster than the Raman instrument but long exposures have not been made on this instrument. The LiF window required constant attention during these experiments because of the deposition of material on the window due to the constant photolysis of the acetylene.

#### 4. Discussion

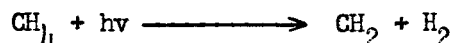
These experiments were preliminary and little can be said at this time concerning the source of the observed emissions, but it is interesting to note that the "Swan bands" of the  $C_2$  radical coincide with the observed region of emission from both methane and acetylene.

McNesby and Tanaka (private communication) have studied the vacuum ultraviolet photolysis of  $C_2H_2$  and  $C_2D_2$  mixtures and have found that the hydrogen formed is mainly  $H_2$  and  $D_2$ . This suggests the occurrence of the molecular elimination of hydrogen,



accompanied by the formation of the  $C_2$  fragment.

If the emission observed from methane is also due to  $C_2$ , it must of course arise from some secondary process. The most important primary process in the vacuum ultraviolet photochemistry of methane is the molecular elimination of hydrogen,



and the formation of the methylene radical,  $\text{CH}_2$ . If  $\text{C}_2$  is formed, it probably arises from subsequent reaction of the  $\text{CH}_2$  radical.

It should also be mentioned that  $\text{C}_2$  "Swan bands" have been observed in absorption at 4.2°K by McCarty and Robinson<sup>5</sup> in the products condensed from methane-argon and acetylene-argon discharges. While the processes occurring in an electrical discharge may be quite different from those observed upon exposure to vacuum ultraviolet radiation, these results do show that  $\text{C}_2$  may be produced from methane and acetylene.

## B. Photolysis of Solids

### 1. Apparatus and Equipment

Vacuum System: The vacuum system was conventional in design; it included suitable pumps, vacuum gauges, valves, liquid nitrogen traps, gas storage bulbs and appropriate dewars for liquid nitrogen temperatures. The half-life measurements were made with the simple dewar shown in figure 2. The dewar for emission studies (figure 3) was larger and had appropriate openings for photolysis of the solid, collection of the emission from the solid, and absorption measurements of excited solids. The flash photolysis apparatus was a commercial unit manufactured by Edgerton, Germeshausen and Grier Inc., and capable of 5000 joules. The flash tubes used were either FX-33 (100 joules) or FX-12 (5 joules). The schematic for this equipment is shown in figure 4.

Chemicals: The water was obtained from quartz equipment, or from the dehydration of reagent grade copper sulfate. Most of the experiments were carried out with water prepared by the latter method because it could be degassed on the vacuum line and would contain a minimum amount of

5. McCarthy and Robinson, J. Chem. Phys. 56 723, 1959.

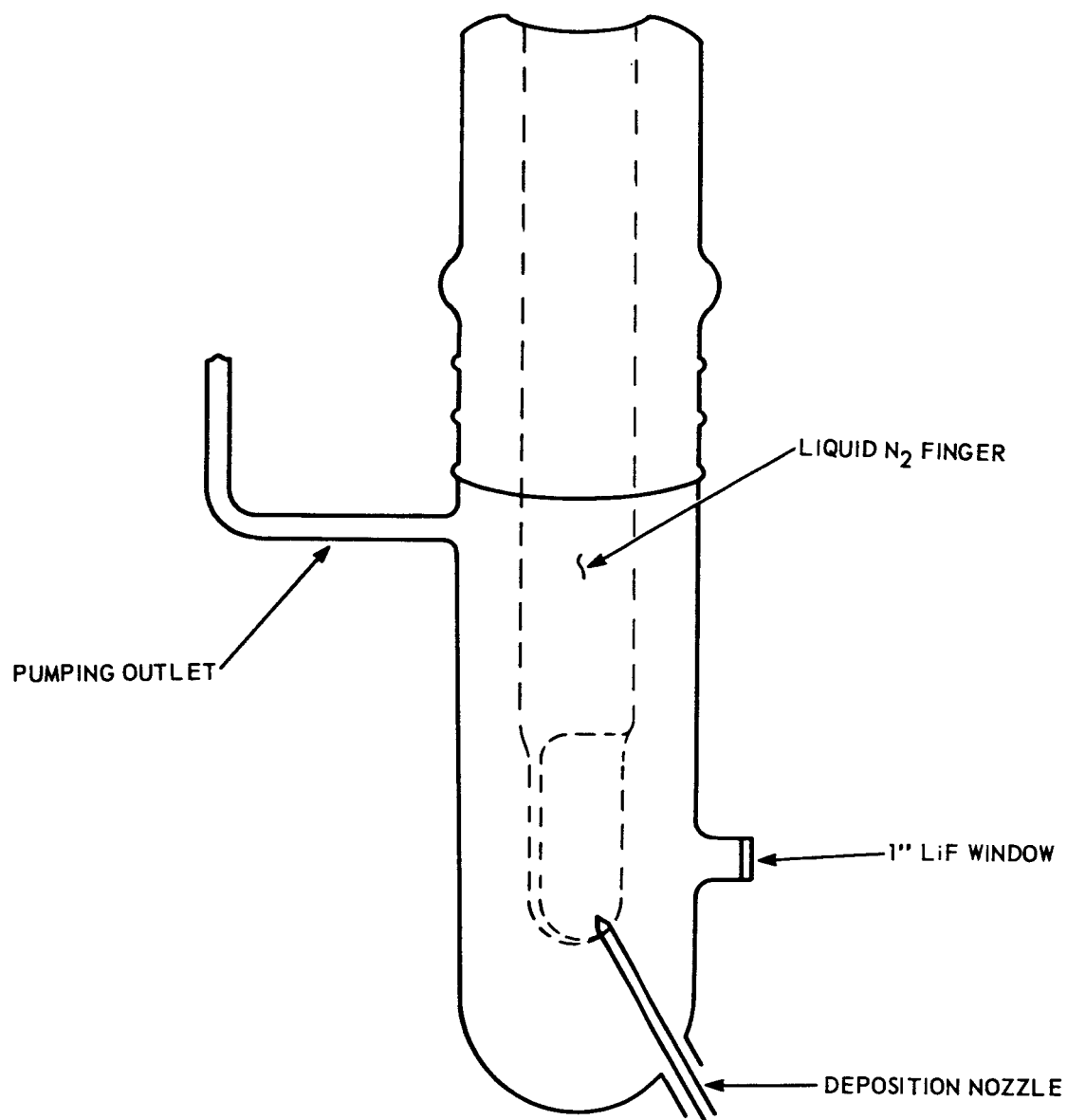


Figure 2. Dewar for Half-Life Measurements

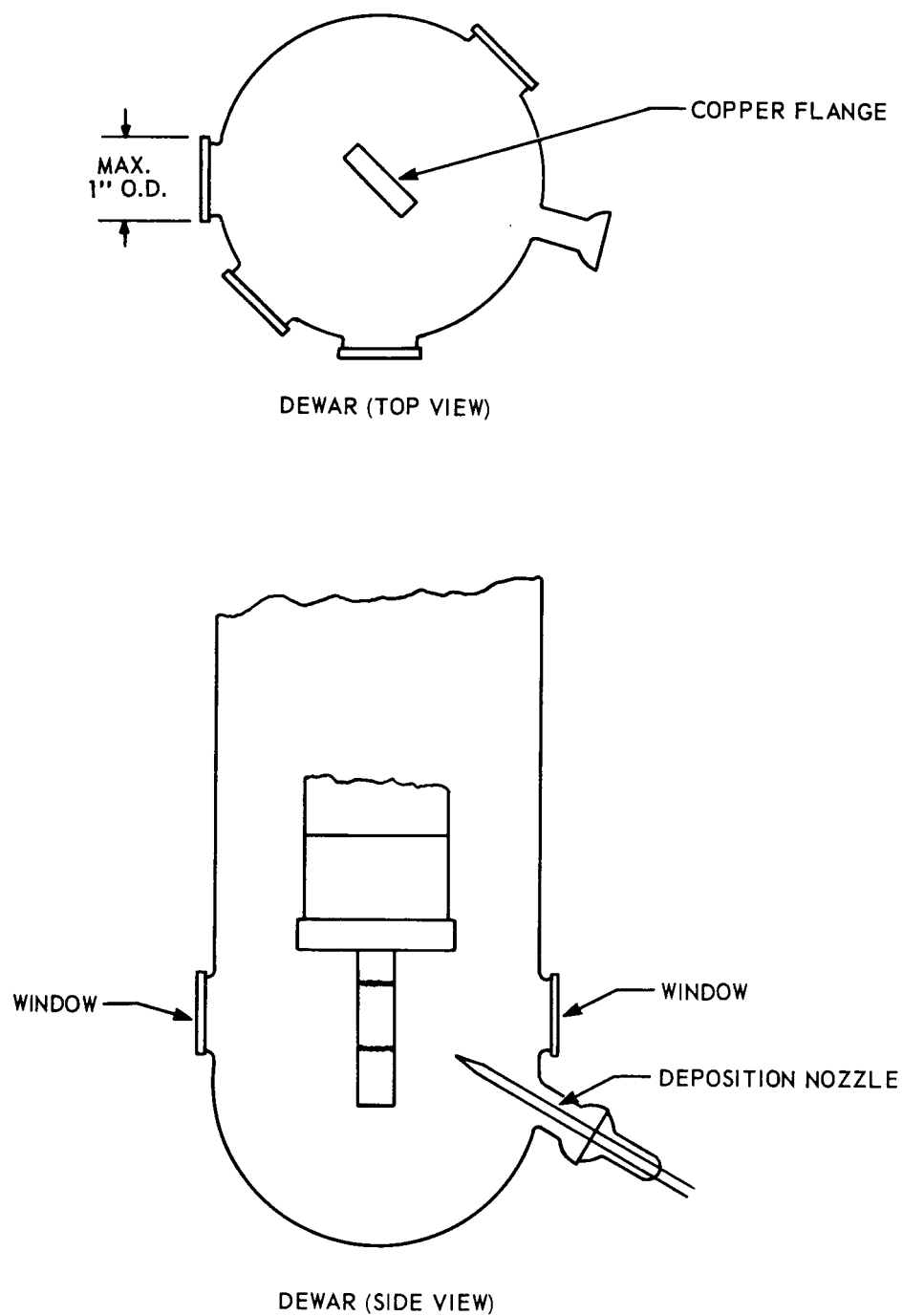


Figure 3. Dewar for Emission Studies

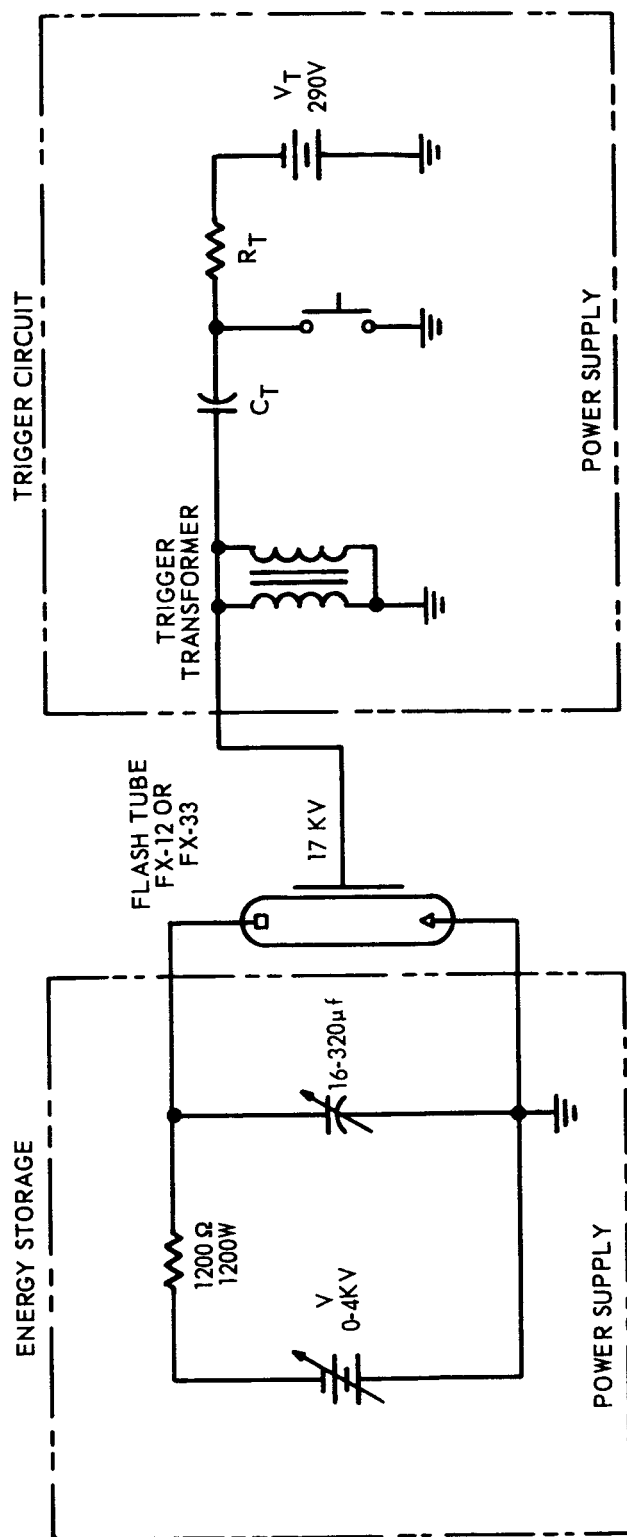


Figure 4. Flash Photolysis Equipment

organic impurities. The ammonia was obtained from Matheson, and dried over metallic sodium. The carbon dioxide and methane were Matheson research grade and they were used without further purification.

Emission Measurements: The spectrographs used in these experiments were Hilger and Watts Models 517 and 498. The half-life measurements were made using a Tektronix Type 545A oscilloscope coupled with an Aminco microphotometer.

## 2. Experimental Procedure

The gas to be studied was deposited on the wall of a liquid-nitrogen-cooled cell. The type of deposit to be studied determined the flow rate of the gas. Flow conditions were established by measuring the pressure of the gas prior to deposition with constant pumping on the dewar.

The emitted light was viewed through quartz windows and was focused by glass lenses on the spectrograph slits. In some experiments the spectrograph was brought to within a few mm of the dewar and no lenses were used. The major portion of the experiments used slit widths of 200 $\mu$ .

Initial experiments used a medium pressure mercury lamp and an appropriate chopping system for collecting the emission. This system was changed to one using a xenon flash lamp operated at 100 joules. A timing circuit connected to the shutter of the spectrograph automatically closed and opened the slits of the spectrograph before and after each flash. A typical flash rate was 1 flash per 10 seconds. Exposures were taken using Kodak 103a0 and 103aF plates with exposure times of 15 to 30 minutes. Standard copper spectra were obtained from hollow cathode lamps (Westinghouse WL-22606). The experimental arrangement is shown in figure 5.



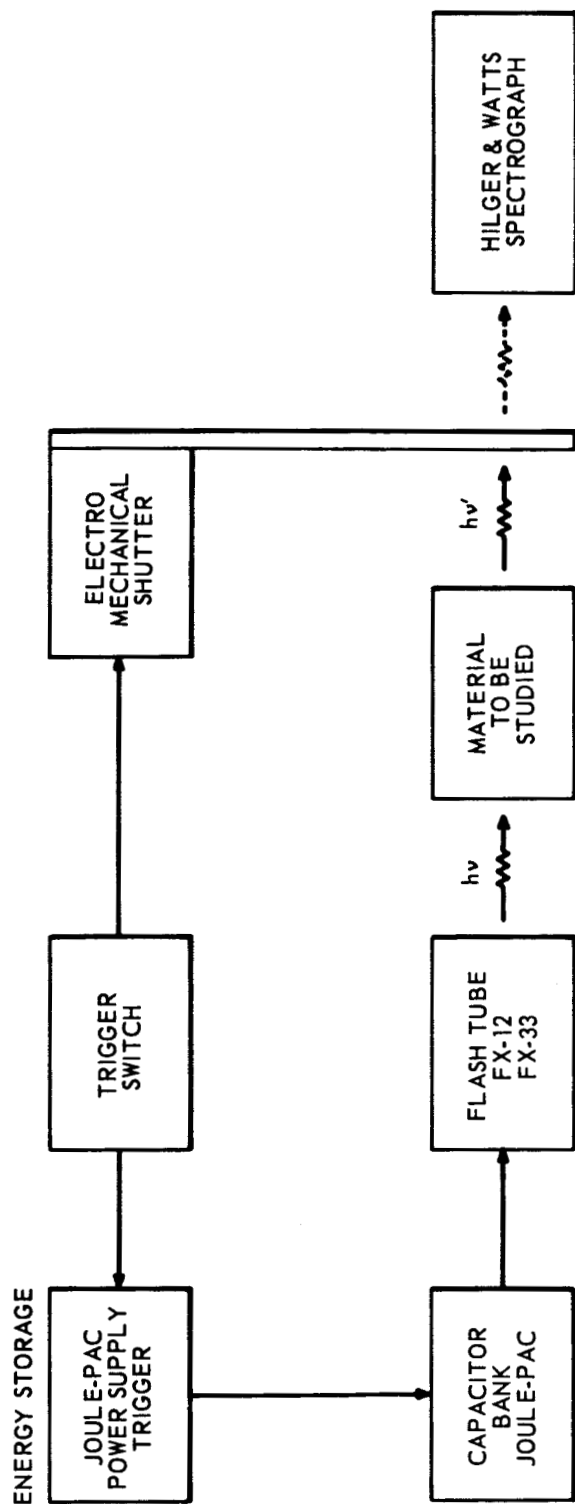


Figure 5. Circuit for Emission Studies

The initial half-life measurements used the 100-watt mercury lamp and a spring-wound shutter. The shutter cut off the radiation and opened the phototube to the emission. The scan rate and voltage were set on the oscilloscope and a picture was taken of the emission decay. Other half-life measurements used the flash photolysis equipment to trigger firing of the FX-12 tube and is shown in figure 6.

Some preliminary experiments were performed to obtain the absorption spectra of the species responsible for the emission in ice. These experiments used behind the deposit (1) xenon flash lamp, (2) tungsten lamp, and (3) deuterium lamp.

### 3. Results

The emission spectra obtained for different water deposits at  $-195^{\circ}\text{C}$  are shown in figures 7, 8 and 9. Because of the diffuse nature of the bands in figure 7, their exact location is difficult to characterize, but they are approximately located at 4025, 4180, 4330, 4460, 4625 and 4690 $\text{\AA}$ . From figure 8 it is shown that not all ice deposits will give rise to all of these bands, but the bands at 4460 and 4625 $\text{\AA}$  are most persistent and frequently obtained from a deposit. A large number of deposits had no band structure, only a continuum as shown in figure 9.

The rate of deposition appeared to affect the production of banded structure in the deposit. Thin deposits prepared by very slow deposition developed the 4460 $\text{\AA}$  and 4625 $\text{\AA}$  bands very easily. Some indication of the development of other banded structure has been observed. Reduction in slit width did not produce the banded structure.

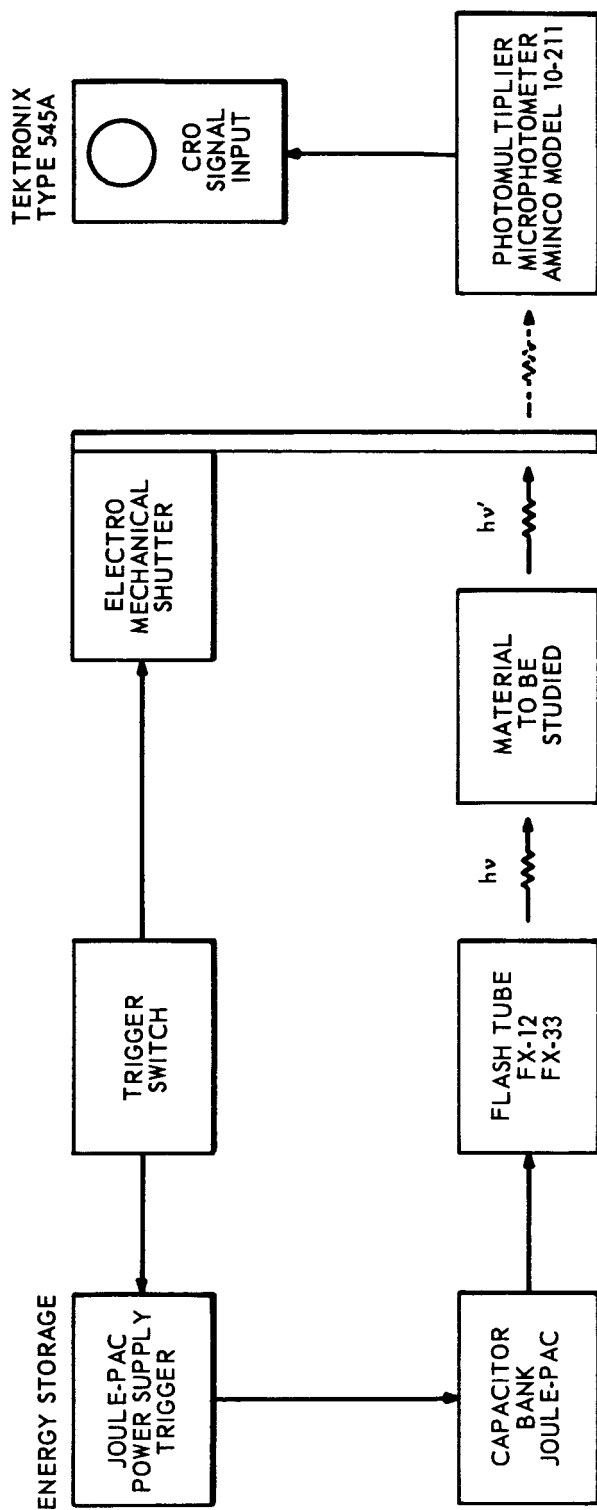


Figure 6. Circuit for Half-Life Measurements

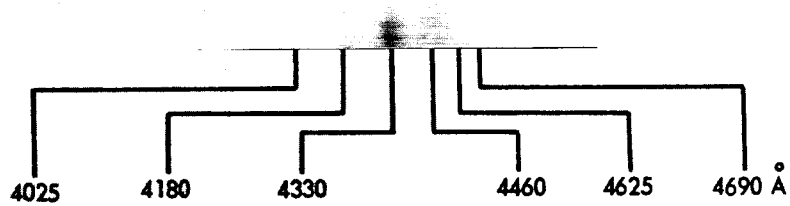


Figure 7. Ice Emission at 77°K

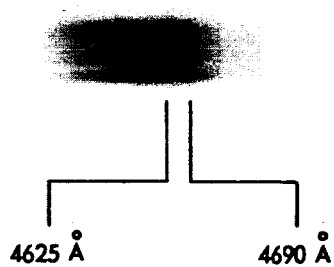


Figure 8. Ice Emission at 77°K

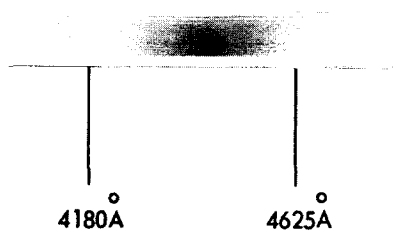


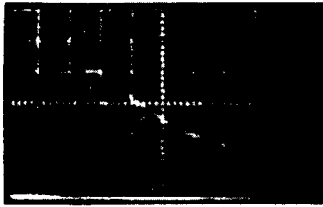
Figure 9. Ice Emission at 77°K

Deposition of water on copper, quartz or Pyrex surfaces did not change the emission of water. However, the intensity of the emission decreased markedly from  $-196^{\circ}\text{C}$  to  $-78^{\circ}\text{C}$  to  $0^{\circ}\text{C}$ .

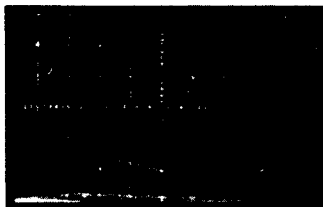
The measured half-life of the ice emission at  $77^{\circ}\text{K}$  was approximately 0.6 seconds. The half-lives, as well as the relative intensity of the radiation, were measured after introducing various filters to remove radiation in different spectral regions. The intensity measured by the phototube was observed to fall off sharply upon introduction of the Corning Pyrex filters CS 0-52 and CS 0-51. The CS 0-52 filter reduced the emission to 10 percent and the CS 0-51 reduced it to approximately 1 percent. The decay curves are shown in figure 10. From the representative transmission curves for these filters and the characteristic output of the Hg lamp used, it can be concluded that the emission was caused primarily by absorption of one or both of the  $3650.15^{\circ}\text{A}$  and  $3663.28^{\circ}\text{A}$  lines of Hg. Blank experiments, conducted with no ice deposited on the cold finger, showed no emission. The emission of ice has also been observed at dry-ice acetone temperature and the half-life was the same as that observed at  $77^{\circ}\text{K}$ .

Preliminary emission spectrum of solid carbon dioxide and ammonia has been obtained and showed some banded structure. There have not been a sufficient number of experiments with these solids for analysis.

The ammonia half-life at  $77^{\circ}\text{K}$  using the xenon flash lamp was approximately 1 second. Added water (1 percent) decreases this half-life to the reported ice emission half-life, with a slight increase in the overall emission. Decay curves of both emissions are shown in figure 11. Elimination of the wavelengths below  $3000^{\circ}\text{A}$  reduced the emission in both cases to



NO FILTER HALF LIFE 0.6 SEC  
RESPONSE  $3.9 \times 10^{-3}$



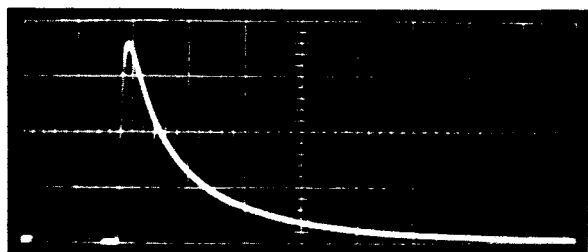
CS 0.52 FILTER HALF LIFE 0.6 SEC  
RESPONSE  $4.8 \times 10^{-4}$



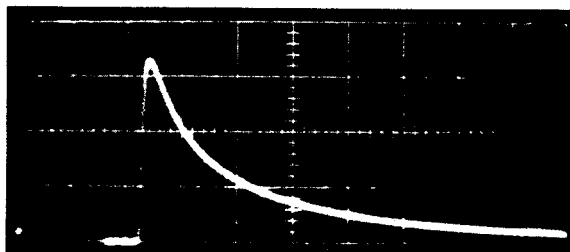
CS 0.51 FILTER HALF LIFE 0.6 SEC  
RESPONSE  $6 \times 10^{-5}$

Figure 10. Water Emission Half-Life at 77°K

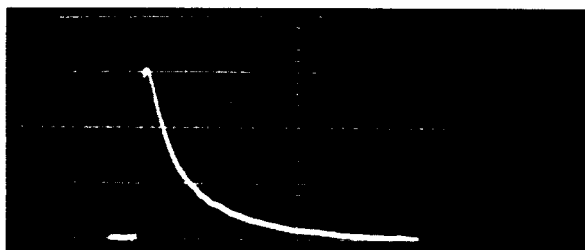




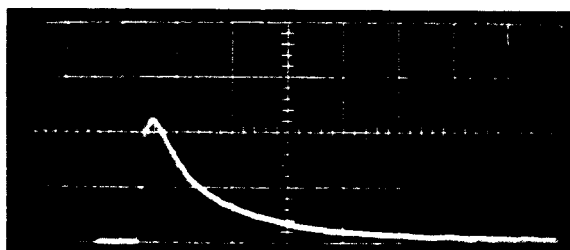
$\text{NH}_3 + 1\% \text{H}_2\text{O}$   
RESPONSE  $10.8 \times 10^{-2}$  HALF LIFE 0.7 SEC



$\text{NH}_3$  DRIED  
RESPONSE  $9.9 \times 10^{-2}$  HALF LIFE 1.0 SEC



$\text{NH}_3 + 1\% \text{H}_2\text{O}$  7-39 FILTER  
RESPONSE  $4.5 \times 10^{-4}$  HALF LIFE 0.5 SEC



$\text{NH}_3$  DRIED 7-39 FILTER  
RESPONSE  $2.3 \times 10^{-4}$  HALF LIFE 0.9 SEC

Figure 11. Ammonia Emission Half-Life at 77°K

less than 0.1 percent. A change of half-life was observed in the  $\text{NH}_3\text{-H}_2\text{O}$  mixture when several filters of a series were used, indicating the presence of  $\text{H}_2\text{O}$ .

#### 4. Discussion

Attempts have been made to control the parameters of deposition so that the conditions for the formation of the banded structure could be determined. The rate and temperature of deposition have been shown to produce different modifications of ice<sup>6</sup> and it is possible that the banded structure arises from a specific modification of ice. These experiments have developed a greater understanding of the behavior of the solid, but have not been successful in reproducing a solid emission as complete as that shown in figure 7.

The strong dependence of the intensity of emission on temperature and the non-dependence of the half-life on temperature as reported above are consistent with an assumption that the luminescence is due to a fluorescence process.

The preliminary absorption experiments were not successful because of the limited number of lamps used and the experiments performed. These absorption experiments appear to offer information directly related to the excited species and independent of the solid. In addition, these experiments could yield information about compounds present in interstellar dust. In particular, the absorption line observed at  $4430\text{\AA}$  for interstellar dust appears most promising because of the emission at  $4425\text{\AA}$  found in these studies.

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6. Lonsdale, D. K., Proc. Roy Soc. A 247, 424 (1958).